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Hexanuclear Dysprosium(III) Compound Incorporating Vertex- and Edge-Sharing Dy_3 Triangles Exhibiting Single-Molecule-Magnet Behavior

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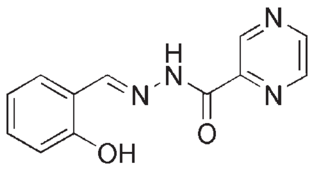
S Supporting Information

ABSTRACT: A unique hexanuclear dysprosium(III) compound with a new polydentate Schiff-base ligand shows complex slow relaxation of the magnetization most likely associated with the single-ion behavior of individual Dy^{III} ions as well as the possible weak coupling between them.

In the past 2 decades or so, the study of single-molecule magnets (SMMs) has been of increasing interest because of their potential practical applications in storage and processing.[1] A large number of compounds displaying this property have been reported since the discovery of the first SMM, Mn_{12} acetate.[2] Especially in recent years, many 4f-based polynuclear SMMs with high energy barriers have been developed, by virtue of the large inherent anisotropy of lanthanide ions.[3] Among them, a peculiar triangular Dy_3 complex has attracted much interest, owing to the unusual slow relaxation behavior originating from the noncollinearity of the single-ion easy axes of magnetization of the Dy^{III} ions lying in the plane of the triangle.[4] This initial communication stimulated much further work in utilizing highly anisotropic Dy_3 triangles as building blocks for creating novel SMMs with higher energy barriers by ourselves and others.[5] By tweaking the reaction conditions, Murugesu and co-workers were able to dimerize the anisotropic Dy_3 building blocks to form a unique Dy_6 SMM exhibiting intramolecular ferromagnetic interaction.[5b] On the contrary, the antiferromagnetic linkage of two Dy_3 building blocks gives a spectacular increase in the temperature at which magnetization slows down, representing a promising strategy to increase the blocking temperature of lanthanide-based SMMs.[5c] Furthermore, ligand oximation can open up the triangle and align the individual spins ferromagnetically as a result of a favorable dipolar interaction, forming a linear trinuclear dysprosium complex showing slow magnetic relaxation.[6] In this respect, the ligand has played a key role in forming clusters with defined geometry and fascinating magnetic behavior. Thus, we designed a new multidentate Schiff-base ligand, (*E*)-*N*′-(2-hydroxybenzylidene)pyrazine-2-carbohydrazide (H_2L; Scheme 1) derived from condensation of salicylic aldehyde and pyrazine-2-carbohydrazide, to construct coordination clusters based on the following considerations: (1) This kind of multidentate ligand has both O and N donors, which can coordinate to two or more metal centers. (2) Similar ligands have been successfully employed to direct the formation of several structurally and magnetically interesting dysprosium SMMs.[3d,7] Herein we report the synthesis, structure, and magnetic properties of a unique hexanuclear dysprosium(III) compound, $[Dy_6(\mu_3\text{-OH})_3(\mu_3\text{-CO}_3)(\mu\text{-OMe})(HL)_6(MeOH)_4(H_2O)_2]\cdot 3MeOH\cdot 2H_2O$ (**1**), which behaves as an SMM showing two clear relaxation regimes.

Scheme 1. Structure of the Ligand (*E*)-*N*′-(2-hydroxybenzylidene)pyrazine-2-carbohydrazide, H_2L



The reaction of $DyCl_3\cdot 6H_2O$ with H_2L in $MeOH/CH_2Cl_2$, in the presence of triethylamine (5 equiv), produces yellow crystals of the hexanuclear complex **1**. The structure consists of two crystallographically unique, but structurally similar, Dy_6 units (denoted as **1a** and **1b**) in the unit cell, as depicted in Figures 1 and S1−S3 in the Supporting Information, SI. Hence, only the details of **1a** are given in the ensuing discussion. The hexanuclear core of complex **1** contains six Dy^{III} ions, which can be regarded as the fusion of three capped triangular Dy_3 motifs, as shown in Figure S1 in the SI. One edge (Dy4 and Dy5) of the regular doubly capped triangle B is connected to Dy6 through a μ_3-OH bridge, forming singly μ_3-OH capped triangle A, while Dy3 of triangle B is linked to Dy1 and Dy2, yielding singly μ_3-OH capped triangle C. The arrangement of triangles B and C is reminiscent of the core topology in the Dy_{10} cluster.[5a] The dihedral angles are 43.428° and 37.160° between triangles A and B and triangles B and C, respectively. A total of six polydentate Schiff-base ligands surround the Dy_6 cluster core and show three different binding modes in its dideprotonated forms (Scheme S1 in the SI). Four methanol molecules, two water molecules, and one CO_3^{2-} anion occupy the remaining coordination sites of Dy^{III} ions. In this complex, the Dy−O and Dy−N bond lengths are in the ranges of 2.1886(110)−2.6227(93) and 2.4575(148)−2.6713(180) Å, respectively. It is interesting to note that the CO_3^{2-} anion coordinated to the three Dy^{III} ions in a less common $\eta^2{:}\eta^2\text{-}\mu_3$ fashion with the third O atom remains uncoordinated. The assignment of a bridging carbonate was

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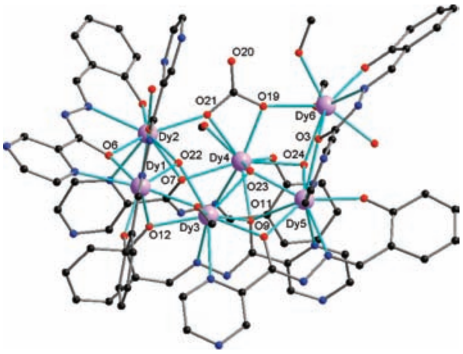

Figure 1. Molecular structure of **1a**. H atoms are omitted for clarity. Color scheme: pink, Dy; red, O; blue, N.

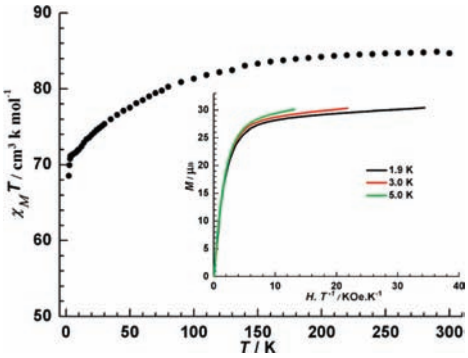

Figure 2. Temperature dependence of the $\chi_M T$ product at 1 kOe. Inset: *M* vs *H*/*T* plots at different temperatures below 5 K.

made based on careful consideration of the diffraction data, which indicated the presence of a trigonal fragment, and a charge balance requiring a dianion in these sites. In particular, IR stretching bands characteristic of coordinated carbonate are observed at 1541 and 1343 cm^{-1} (Figure S4 in the SI).[8] Nitrate was not present in the reaction at any stage; therefore, it appears that atmospheric CO_2 has been incorporated into the structure, thus templating further aggregation and growth of the cluster.[9]

In addition, three noncoordinated methanol molecules and two water molecules of crystallization (per unit cell of **1**) are located in the crystal lattice. Finally, compound **1** is a hydrogen-bonded dimer, with the shortest Dy···Dy distance within the dimer 8.2426(11) Å (Figure S5 in the SI).

The direct-current (dc) magnetic susceptibility studies of **1** were carried out in an applied magnetic field of 1000 Oe in the temperature range 300−2 K. The plot of $\chi_M T$ vs T, where χ_M is the molar susceptibility, is shown in Figure 2. The observed $\chi_M T$ value at 300 K of 84.8 cm^3 K mol^{-1} corresponds exactly to the expected value of 85.02 cm^3 K mol^{-1} for six uncoupled Dy^{III} ions ($S = {}^5/_2$, $L = 5$, ${}^6H_{15/2}$, $g = {}^4/_3$). $\chi_M T$ gradually decreases until 50 K and then further decreases to reach a minimum of 68.6 cm^3 K mol^{-1} at 2 K, which is probably ascribed to the progressive depopulation of excited Stark sublevels,[10] and the shoulder at low temperatures might suggest a competition between the ligand-field effect and possible ferromagnetic interactions between the Dy^{III} ions.[7,11]

The *M* vs *H*/*T* (Figure 2, inset) data at different temperatures reveal a rapid increase of the magnetization at low magnetic fields, which eventually reaches a value of 30.9 μ_B at 1.9 K and 7 T without any sign of saturation. This value is lower than the expected saturation value of 60 μ_B (for six noninteracting Dy^{III} ions). This difference is most likely due to anisotropy and the crystal-field effects[4] at the Dy^{III} ion, which eliminate the 16-fold degeneracy of the ${}^6H_{15/2}$ ground state.[12] The nonsuperposition of the *M* vs *H*/*T* data on a single master curve suggests the presence of significant magnetic anisotropy and/or low-lying excited states in compound **1**.

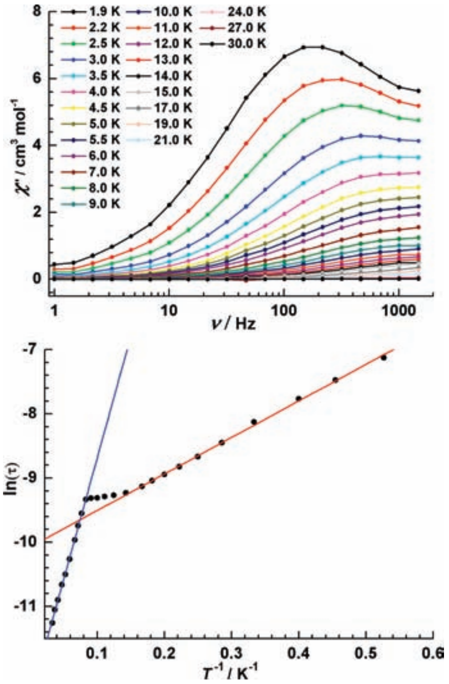

Figure 3. Frequency-dependent out-of-phase ac susceptibility of **1** below 30.0 K under zero dc field (top). Magnetization relaxation time, ln τ, vs T^{-1} under zero dc field. The solid line is fitted with the Arrhenius law (bottom).

The dynamics of the magnetization were investigated using alternating-current (ac) susceptibility measurements, with the results in the zero static field and a 3.0 Oe ac field oscillating at various frequencies from 1 to 1500 Hz given in Figures 3 (top) and S6 and S7 in the SI. At temperatures below ~30 K, a frequency-dependent out-of-phase (χ'') ac signal reveals the onset of slow relaxation of the magnetization that is typical of SMM behavior. Analysis of the Cole−Cole plots (Figure S8 in the SI) shows a nearly semicircle shape with the α parameter close to zero (single relaxation process) for the temperature range 3−7 K, while below 3 K, α increases, suggesting a wide distribution of τ.[13] The relaxation time was extracted from the frequency-dependent data between 1.9 and 17 K, and the Arrhenius plot obtained from these data is given in Figure 3 (bottom). It is noteworthy that two relaxation regimes are clearly visible, with a transition between them corresponding to an energy gap (Δ) of 5.6 and 37.9 K and preexponential factors (τ_0) of 4.2×10^{-5} and 3.8×10^{-6} s for the low- and high-temperature domain, respectively. The interesting magnetic behavior that has been increasingly identified in weakly coupled dysprosium compounds can presumably be attributed to the large intrinsic magnetic anisotropy of the Dy^{III} ions.[14] The magnetic anisotropy of a polynuclear system depends not only on the individual anisotropies of the metal ions but also on the relative orientation of the local axes.[15] In addition to this, the exchange interaction between the lanthanide ions is also expected to contribute to the relaxation.[16] The slow relaxation is probably dominated by the single-ion behavior of individual Dy^{III} ions at the higher temperatures, while the weak coupling with neighboring Dy^{III} ions might become important at low temperatures.[17] However, it has to be mentioned that a conclusive answer on this point might only come from ab initio calculations and single-crystal magnetic measurements. In addition, ac susceptibility measurements under applied dc fields have been performed in order to suppress possible fast zero-field quantum relaxation (Figures S9 and S10 in the SI). The results showed that the application of these fields has practically no effect on the dynamics, suggesting that the tunneling in zero field is less efficient in this complex above 1.9 K.[5c,7]

In summary, a new polydentate Schiff-base ligand has been successfully employed to assemble with Dy^{III} ions, affording a hexanuclear Dy^{III} cluster with an unprecedented topology based on vertex- and edge-sharing Dy$_3$ triangle units. The Dy$_6$ complex behaves as an SMM with a frequency-dependent out-of-phase signal. The two relaxation regimes observed in this compound might associate with single-ion relaxation of Dy^{III} ions and the weak coupling between them at high and low temperatures, respectively. However, a joint contribution, combining the experimental efforts with doping studies and theoretical calculations, is required to better understand the underlying mechanism in polynuclear lanthanide complexes.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format, detailed experimental procedures, and additional structural and magnetic data for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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